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Effects of Oxygen on the Sulphur and Heating Value of Coal

EFFECTS OF OXYGEN ON THE SULPHUR AND HEATING VALUE OF COAL

BY

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INTRODUCTION.

The question of the deterioration of coal in storage and also the closely connected subject of spontaneous combustion in storage are old ones. The literature on these two subjects is very extensive and hard to get at, but a good summary of the work on spontaneous combustion is given in the appendix of Parr and Kressman's[1] bulletin on, "The Spontaneous Combustion of Coal". The first part of the work outlined in this paper was an attempt to find out what part iron sulphide had in the spontaneous combustion of coal but this work was stopped before anything definite was decided upon. The second part of this work dealt with the change in calorific value after treatment with oxygen at a pressure of 20 to 25 atmospheres.

The opinions upon the effect of pyrite on spontaneous combustion are widely different and a number of them are exactly contradictory. It seems to be a generally accepted view that the pyrite is very appreciably oxidized but its effect upon spontaneous combustion is an open one. The FeS_2 which has a heating value of 2132 B.T.U. per pound when burned to SO_2 may be changed to $Fe\ SO_4$ or Fe_2O_3 and SO_2 and so not only is the calorific of FeS_2 lost but two very undesirable ash constituents are formed. The oxidation of pyrite might aid spontaneous combustion by its chemical action or it might simply be mechanical. The oxidation to sulphate might cause cleavage in the coal and thus expose a larger surface to the oxidizing action. Closely associated with FeS_2 are sulphides of calcium and magnesium and if these sulphides are oxidized during storage to sulphates and oxides, their value as heat producers is destroyed.

Parr and Francis[2] have shown that the coal substance begins to oxidize at about 135°C when in air. Quoting from this bulletin,"Since coal is a rather poor conductor of heat the major part of the heat generated within the pile, will be retained and from the calculation of the heat generated by the pyritic oxidation, it may seem that a sufficient quantity of heat was liberated to bring the coal up to this temperature of 135°, at which active oxidation of the carbonaceous materials begins."

EXPERIMENTAL.

I. Oxidation of $Fe\ S_2$.-- In the work outlined here the soluble sulphate was extracted before and after oxidation, and in this way an increase in oxidized sulphur was determined. This did not give an absolute value of the soluble-sulphur but it gave a good relative test. Parr and Kressman[1] and Porter and Fieldner[4] suggested 1 % HCl or 2% Na_2CO_3 as digesting agents but it was found here that HCl gave more consistent results although not so high as Na_2CO_3. The digestion was done in a round bottom flask with an upright condenser and the liquid was allowed to boil gently. Considerable trouble was experienced in washing the coal free from the digesting liquid at the end of the operation. Warm water was used as a wash liquid. Air, dried over H_2SO_4 was used as the oxidizing agent. The coal finely divided was spread out in a glass tube about 30 inches long and one half inch in diameter. This was plugged loosely with glass wool at the outlet end and contained a tight fitting cork carrying a short glass tube at the inlet. The tube containing the coal was placed in a glass tube about 3 inches

Moisture	Length of oxidation
9.23	72. hrs.
2.17	
6.16	165 hrs.
1.34	
6.04	168 hrs.
1.52	
2.56	100 hrs.
1.70	

in diameter and 28 inches long which was loosely plugged with glass wool at intervals along its length. This gave an air jacket around the tube containing the coal and the glass wool formed a slight resistance to the air. Thermometers were introduced into this air jacket through holes near each end. The dried air was passed slowly through the tube containing the coal, while air from the compressor was circulated freely through the jacket to remove any heat which was given off as a result of the reactions. This gave a constant temperature within 2 or 3 degrees.

The sulphur was determined in the usual way by precipitating with 10% $BaCl_2$ in acid solution after oxidizing the iron with bromine and subsequent removal of the iron by NH_4OH. The purity of some of the sulphate was tested according to Talbot's Quantitative Chemical Analysis, page 32, and it was found to contain only a trace of impurity.

Results.

Table I. Oxidation of Pyrite

	Sample No.	Wt. Of Sample Tested	Mesh	Digested in	Amt. of Digesting Agent	Percent Sulphur (dry)
Before oxidation	3	5 g.	100	1% HCl	100 c.c.	.04995
After " "	3	5 "	100	" "	" " "	.08311
Before " "	4	5 "	150	" "	" " "	.05685
After " "	4	5 "	150	" "	" " "	.05649
Before " "	5	5 "	150	" "	" " "	.08246
After " "	5	5 "	150	" "	" " "	.08890
Before " "	6	5 "	150	" "	" " "	.03076
After " "	6	5 "	150	" "	" " "	.03076

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]

The coals were all Illinois coals and were sampled at the University coaling station. Number 3 and 5 were sampled within a week after being mined but numbers 4 and 6 had been stored out of doors for several weeks. A few grams of $Fe\ S_2$ were added to coal number 5. The range of temperature within the tube was between 25° C and 28° C, and the air was bubbled through at about 140 bubbles per minute.

II. Effect of Increased Temperature.

An attempt was made to carry on this oxidation at different temperatures. For this the outer glass tube forming the air jacket was replaced with a cast iron pipe and the space between the two tubes was filled with sand. Three Bunsen burners were used to raise the temperature and very good control of temperature could be obtained in this way but it was not allowable to leave these burning over night so the apparatus was not used. Next, the bottom was cut off of a large glass bottle and the bottle placed on a piece of plate glass. A 50 candle-power carbon lamp was introduced into the bottle through the stopper. This also gave a good temperature control as a temperature of 50° C was kept constant within one degree for several days, but when some coal, powdered to 150 mesh, was introduced the temperature slowly rose to 58° C. It took about 14 hours for this rise to take place but then it remained practically constant. Just at this time the work was interrupted and when it was again taken up it was from an entirely different standpoint.

Discussion of Results.

These results show that the $Fe\ S_2$ is quite appreciably oxidized in the air although no ignition of sample took place as noticed by Parr and Kressman,[1] probably because any heat formed was removed by the circulating air both in the jacket and over the coal. Any rise in temperature would probably increase the rate of oxidation and in storage this heat would not be removed and so would greatly increase the oxidation. Moist air would also probably cause an increase as shown by a number of writers.. It seems likely that if a piece or particle of coal became covered with an oxidized layer or if the pyrite became covered in this way the rate of oxidation would be greatly decreased because of this covering keeping out the air. This might explain the lack of increase in oxidized sulphur in coal #4. It would generally be expected that a coal more finely divided would oxidize more easily than one not so finely divided, but beyond 50 or 60 mesh this did not seem to be true. If the air was bubled through the coal and so be mixed intimately, this would probably prove true, but here the air seemed to cause a packing or caking near the surface and this probably prevented an intimate mixture. Lamplough and Hill[5] state that a large amount of CO_2 is given off during oxidation and they explain it by the following equations:

$$4\ Fe\ S_2 + 15\ O_2 + 8\ H_2O \text{ ------- } 2\ Fe_2O_3 + 8\ H_2SO_4$$

$$8\ H_2SO_4 + 8\ CaCO_3 \text{ -------- } 8\ CO_2 + 8\ CaSO_4 + 8\ H_2O$$

But their results show that a coal containing only a small amount of pyrite gives off as much CO_2 as a coal containing a large

amount of pyrite although the carbonaceous matter is practically the same in both cases.

III. Change in Heating Value.

In a few experiments carried out at the University of Illinois it was found that after treating powdered coal with oxygen at about 25 atmospheres, the heating value was increased. The coal took up an appreciable weight of oxygen and if the resulting heating value was corrected for this increased weight an actual gain in B.T.U. was found. This result was so unusual that it was thought best to try to verify it. All work up to this time had shown an apparent decrease in B.T.U. upon storage. Parr and Wheeler[7] found that the calorific value apparently decreased rapidly the first week and then more slowly for an indefinite period. Various other writers have found similar results although some of the results seem very much exaggerated. Heat is undoubtedly given off during oxidation as has been shown by Parr and Kressman[1], Lamplough and Hill[5] and others, but this heat is lost through radiation and should represent the heat lost as a fuel. If there is any heat of absorption or adsorption we can expect an increase in temperature which might not be a part of the calorific value of the coal. Lamplough and Hill[5] report that from 2.9 to 3.8 calories are evolved per cubic centimeter of oxygen taken up. This would include heat of reactions and heat of adsorption. An attempt was made in this work to measure any heat of absorption but it was not successful. It will be described later.

The coal was air dried and ground to pass a 60 mesh screen and a sample weighing from twelve to sixteen grams was used in each case. The sample contained in a weighing bottle was treated in a Parr Illium bomb with from 20 to 25 atmospheres of oxygen and left for different periods. Any increase in weight after treatment was noted and this increase was taken as the weight of oxygen which was taken up. The moisture and heating value were determined before and after treatment. The heating values were determined in a Parr adiabatic calorimeter in which checks within 10 B.T.U. in twelve thousand were obtained. The moisture was determined in an atmosphere of carbon dioxide at a temperature of 104° C, although air was used instead of carbon dioxide in a few cases. The coals used were two Illinois coals, one anthracite and one Pocahontas. The Illinois coals were low in sulphur and ash; they were sampled while fresh and kept tightly stoppered. The anthracite had been stored in an open bin for about six months and the Pocahontas had been stored in a concrete basement for about the same length of time. It was impossible to get any samples any fresher than these because of the shipping difficulties.

Table II. Effect of Oxygen Treatment.

Coal							Moisture	
Laboratory No.	Time in hours	Pressure: Atmospheres	Ash	Sulphur	Oxygen taken up	Percent Oxygen taken up	1	2
4210[1]	147	24	5.34	.7903	.0580 g.	.79	4.41	4.87
4210	260	20	5.34	.7903	.1226 "	.96	4.68	4.95
4210	260	20	5.34	.7903	.1226 "	.96	4.68	4.72
4211[2]	118	25	7.34	.7788	.0587 "	.556	5.00	4.12
4211	260	25	7 34	.7788	.0865 "	.86	5.49	5.50
4211	86	25	7 34	.7788	.0391 "	.454	5.23	5.29
4213[3]	74	25	10.12	1.15	.0185 "	.165	1.64	1.70
4214[4]	53	25	4.94	.559	.0140 "	.146	1.00	.98

1. An Illinois coal from Danville
2. An Illinois coal from Danville
3. Anthracite.
4. Pocahontas.

Discussion of Results.

The results obtained do not agree with the work mentioned above, that the calorific value increased with this treatment. The second test on coal #4210 is the only one to show an increase and this increase is easily within experimental error. In this determination the moisture was determined at 104° C in an atmosphere of air and an increase of .27 % was found. The moistures were run at the same time so as to have exactly similar conditions. When this same sample was used for a moisture determination in an atmosphere of carbon dioxide there was only .04 % increase which is not to be considered as a change. Using these constant moisture values the calorific value showed an actual loss of 28 B.T.U. The first samples of #4210 and #4211

Califorific Value in B.T.U. per pound.

1 (Dry)	2 (Dry)	Corrected for Oxygen	Apparent Difference	Real Difference
13567	13440	13548	-127	-19
13607	13482	13613	-125	+6
13607	13449	13579	-158	-28
13671	13548	13624	-123	-47
13743	13390	13506	-353	-237
13704	13199	13259	-505	-445
13505	13467	13500	-38	-5
14756	14711	14733	-45	-23

were run in air with an increase in one case and a decrease in the other. It was not possible to check these results in carbon dioxide. A number of determinations were run both in air and carbon dioxide to see if any difference was found and the results with carbon dioxide gave very good checks but the results in air gave a fairly wide range of results. Some coals gained moisture under this treatment with oxygen, some lost moisture and some remained constant if air was used as a drying agent. The same results were obtained by Parr and Wheeler[7] in air drying coal. This might be caused by the fact that some of the coal substances are oxidized and thus become more volatile.On the other hand the oxygen might fix some of the hydrocarbons and air increase or aid the fixation thus preventing such a large amount of volatile being given off at 104° C. Anything which is given off up to 104° C is called moisture although an appreciable amount of hydrocarbons might be given off and these oxidized products might easily be given off in a stream of oxidizing gas such as air while carbon dioxide would not cause any change.

In the columns in Table II, head 1 are given values before the treatment with oxygen and under heading 2 are given results after treatment with oxygen. Under the heading "apparent difference" is given the apparent loss in B.T.U. This is the difference between column 10 and 11 and this is the difference usually given in work of this kind. Under the heading "actual difference" is given the difference between the heating value before treatment and the heating value after treatment, with the correction for the amount of oxygen taken up. Any oxygen taken up

gives an increase in weight but reduces the ratio of combustible to oxygen. The amount of oxygen taken up is a function of the time of exposure, oxygen being taken up much more rapidly at first. In the first two cases an increase of almost double the time gave an increase of about one fourth in oxygen taken up. In the second case an increase of almost double the time gave an increase of about one and one half and three times in the length of treatment only gave increase of one fourth and one and three quarters respectively, in amount of oxygen taken up. The low rate of absorption in the cases of #4213 and #4214 is probably due to the fact that after being stored for six months they had become almost saturated with oxygen.

IV. Evacuation Treatment.

An attempt was made to show that the oxygen taken up was not chemically combined. To do this a weighed amount of 60 mesh coal, about 15 grams, was subjected to a vacuum of about 6 cm. of mercury and left there until the mercury column became stationary. Any change in weight was noted and the moisture and calorific values were determined. Then the same was treated with 20 to 25 atmospheres of oxygen and any change in weight heating value or moisture was noted. Then it was subjected to the vacuum treatment as before and any change in weight, heating value or moisture again determinedIt usually took three or four days for the evacuation in each case and about two days for the oxygen treatment.

Table III. Vacuum Treatment.

	After Treatment under 6 cm. Vacuum.			After Treatment under 25 Atmospheres of Oxygen			Second Treatmant under Vacuum.		
	Change in wgt.	Change in Moisture	Change in B.T.U.[1]	Change in Weight	Change in moisture	Change in B.T.U.[1]	Change in Weight	Moisture Change	Change in B.T.U.[1]
1	-.059%	+.02%	+10	+.201%	+.01%	+23	.56%	-.55%	-80
2	-1.4%	-.92%	-357	+.212%	-1.16%	-401	2.1%	-1.29%	-.282

1. All B.T.U. calculations are the dry basis and corrected for any change in weight. These are the same as coal #4211. They are samples of Illinois coal.

A lack of time prevented more work along this line and the above data is not complete enough to allow any conclusions to be drawn. The losses given in the table are referred to the original coal before treatment. The fact that more substance is pulled out during the second evacuation, than the oxygen put in might be due to the fact that the oxygen had increased the hydrocarbon gases in the coal and these were pulled out in addition to the oxygen. It might also be due to breaking up of some tightly held water. If the water is held in the coal mass as in the form of a jell, the pressure of the oxygen might change their equilibrium and so leave an additional amount of moisture free and this would be pulled out during the second evacuation. This would also explain the decrease in moisture. The increase in B.T.U. after the second evacuation in Table III is not easily explained.

V.Heat of Adsorption.

Lamplough and Hill[5] showed that about 3.6 calories per c.c. of oxygen absorbed were given off. It was thought that possibly part of this heat was heat of absorption and an attempt was made to measure this heat of absorption. The procedure was as follows: A weighed amount of 60 mesh coal, about five grams, was placed in a glass bulb and the bulb sealed. The bulb was placed in the bomb of the Parr adiabatic calorimeter and a weight of about 600 grams was suspended from the cover of the bomb by a piece of the ignition wire used in this calorimeter. About 25 atmospheres of oxygen were used in the bomb. When a current was passed through the wire it broke causing the weight to fall and break the bulb. Out of several attempts a rise in temperature after 30 to 40 minutes was found in only two cases and in one of these the coal took fire and about half of it burned to coke while the remainder appeared to be unchanged. The other case gave a rise of .14°C but it was probably due to a piece of the fuse wire dropping into the coal. This rise in temperature is probably so slow at ordinary temperatures that it can be measured with great difficulty.

Conclusions.

It seems evident that the FeS_2 in coal is oxidized by air and that considerable heat is given off. The conditions in these tests probably gave an effect equal to several weeks storage because of the powdered condition of the coal and oxidation was accelerated by a continual supply of fresh air. On the other

hand the rise in temperature due to the oxidation would not be counteracted as here and the heat would remain in the pile to further increase oxidation instead of being removed by the air jacket. The method of extraction shows what might happen if coal were stored under water and a water containing considerable carbonate was used. A long storage would remove the sulphates and thus do away with a great ash former and heat user. This would give an increase in the ratio of combustible to ash and give an increased calorific value. When FeS_2 is oxidized it causes the coal to break up and thus exposes a much greater area to the oxidizing agent so that probably its effect may be as much mechanical as chemical. FeS_2 is not essential to spontaneous combustion because coals almost free from it are sometimes spontaneously combustible but it seems likely that FeS_2 helps bring the coal substance to its ignition temperature.

The fact, stated above, that after treatment with oxygen at 25 atmospheres pressure, the coal gained in calorific value was not substantiated. The loss in calorific value does not seem to be as great as generally supposed if any account of the oxygen added is taken. The heating value seems to decrease rapidly during the first period but then slowly decreases although the point where no more oxygen will be taken up was not found.

SUMMARY.

Sulphur is oxidized in the air to an extent which might materially increase the heat to the kindling temperature of

the coal substance.

Coal does not gain in calorific value when treated with oxygen at 20 - 25 atmospheres pressure.

After treatment with oxygen at these pressures an increased amount of substance may be taken out by vacuum. This might indicate an oxidation or a change in the equilibrium in the colloidal solution.

Any heat of adsorption is too slow to be measured by ordinary calorimetric means.

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